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Qualitative and quantitative evaluation of epoxy systems by Fourier transform infrared spectroscopy and the flexibilizing effect of mercaptans

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Abstract: Epoxy systems are widely applied as adhesives in the aerospace industry. They have excellent adhesion properties, however, being thermosetting, epoxy systems show fracture brittleness characteristics. Polysulfide and polymercaptans are good options to increase the flexibility of the epoxy adhesive. Thermal analysis techniques are generally used to evaluate the curing degree of epoxy systems. In most cases, when infrared (IR) analysis is used, it is employed qualitatively. This paper presents the reaction study of a DGEBA epoxy prepolymer with diethylenetriamine (DETA) and linear and branched dodecyl mercaptans as flexibilizers. Conversion data and curing time were assessed qualitatively and quantitatively by Fourier Transform Infrared Spectroscopy (FT-IR) in the medium infrared region (MIR) and in the near infrared region, using near infrared reflectance accessory (NIRA). NIRA methodology showed satisfactory results, with errors between 3 and 7%, especially in samples with lower amine contents. Mechanical tests confirmed the flexibilization of the cured epoxy system by the addition of mercaptans, indicating a lower crosslinking degree in the matrix. Young's modulus (E) significantly decreased from 2017 MPa to 578 MPa with the addition of approximately 20 wt% of normal dodecyl mercaptan to the epoxy system.

Key words: epoxy resin, FT-MIR, mechanical properties, mercaptans, NIRA.

INTRODUCTION

Epoxy resins have been widely used as engineering adhesives. They have good thermal stability and excellent adhesion properties, however, being thermosetting, they show fracture brittleness characteristics. This factor can become a problem in many applications (Sun et al. 2014).

Epoxy resins provide adhesion of metal surfaces in aerospace applications. However, due to the efforts suffered by the intense acceleration of an aircraft, among other factors, the brittleness of cured thermosetting epoxy polymers may lead to crack formation and

propagation. Cracks may weaken the metal/resin and metal/metal bonds and cause detachment of aircraft parts. There are several alternatives to increasing fracture resistance of epoxy systems, including the use of rigid particles (such as TiO_2 , SiO_2 , Al_2O_3 and carbon tubes) in the epoxy matrix. Addition of nanoparticles of TiO_2 , for example, can simultaneously improve the rigidity and toughness of the epoxy system (Carballeira & Hauptert 2010).

The addition of rigid compounds to epoxy resins, however, is not a viable alternative in aeronautical applications due to the low temperatures an aircraft has to endure. At low

temperatures and in circumstances of significant temperature fluctuations, rigid compounds not only fail to increase the strength of the epoxy compounds but also generate stress points in the matrix, facilitating crack formation and propagation (Sun et al. 2014).

Soft fillers, such as high-impact polystyrene (HIPS), Styrene-ethylene-butadiene-styrene (SEBS) copolymer, Styrene-butadiene-styrene (SBS) copolymer, among many other thermoplastics, block copolymers and rubbers, are potential toughening agents. They have similar thermal and physical properties of epoxy polymers and have been vastly studied as well (Serrano et al. 2004, Pandit et al. 2014, George et al. 2015, Wang et al. 2016, Dadfar & Ghadami 2013, Tang et al. 2013, Rico et al. 2012, 2005, Chen et al. 1994).

Flexibilizing agents and toughening agents are fundamentally different species. Toughening agents and cured epoxy resin are incompatible, while flexibilizing agents are significantly compatible with cured epoxy resins and act as plasticizers. The plasticizing effect of flexibilizing agents results in the decrease of tensile and shear properties, and the increase of the cleavage strength. Component migration is a common problem encountered with the use of plasticizers in cured epoxy systems. The use of a particularly compatible flexibilizer that has a molecular weight large enough to induce chain entanglements with the cured epoxy resin, and that has functional groups that can co-cure with the epoxy resin may reduce the leaching out of lower molecular weight polymers carried by the plasticizer (Hartshorn 1986).

Polysulfide is an option to increase the flexibility of the epoxy adhesive. Terminal mercaptan groups react with the epoxide resin groups and are incorporated into the resin matrix (Andrade et al. 2008). However, it is not

produced in Brazil, which motivates the search for simpler and lower cost solutions.

Andrade et al. (2008) studied the flexibility of epoxy adhesives with the addition of mercaptan groups (CAPCURE) by conventional techniques of infrared spectroscopy using transmission mode and thermal analysis. The use of mercaptans (-SH) may be an alternative to improve flexibility and reduce brittleness of epoxy resins. Furthermore, the study of the reaction of epoxy prepolymer (EP) with mercaptans might be necessary to understand the contribution of this system.

There are several studies approaching the cure of epoxy resin using different curing agents (CA) (Andrade et al. 2008, Wang et al. 2018, Krauklis & Echtermeyer 2018, Iheaturu & Ofoegbu 2018, Konuray et al. 2017, Kiran & Gaur 2016, Yamasaki & Morita 2012, Hardis 2012, González et al. 2012, Lakshmi et al. 2010, Raditoiu et al. 2009, Fang et al. 2008, Costa et al. 2005, 1999, Romão et al. 2004, 2006, 2003, Zeiss 2018, Guilherme et al. 2017, Strzelec et al. 2012). The majority of the studies approaches compositions with amines.

Researchers studied the effect of imidazole-based curing agents in epoxy systems used in the automotive industry (Wang et al. 2018, Fang et al. 2008). Thermal analysis reveals rapid cure at 120°C and higher glass transition (Wang et al. 2018). Curing reactions were evaluated by the FT-IR spectrometric changes (presence or absence of bands) in the MIR region using transmission mode. Samples were prepared as KBr pellet (Fang et al. 2008). The appearance of OH bands around 3200 cm^{-1} , the disappearance of epoxide ring bands around 920 cm^{-1} and the transformation of the imidazole primary amine groups into secondary amine groups also around 3200 cm^{-1} were observed. It is possible that KBr intrinsic humidity interfered with the proper assignment of the bands resulting from the curing reaction, especially in the region 3200-3300 cm^{-1} . A FT-IR

reflection methodology, without the use of KBr, could have been evaluated.

It is important to choose well both the resin and hardener for each application in order to obtain the desired properties. Amines are excellent performing CA for diglycidylether based epoxies. The linkage between the aromatic rings and the oxygen atoms (ether group) in DGEBA has a strong electron-withdrawing effect that makes the oxirane group highly reactive towards nucleophilic compounds like amines. Diamines and triamines are highly reactive due to the high nucleophilicity of the nitrogen atom of the amino groups, especially aliphatic amines (González et al. 2012).

Since there are several CA and flexibilizing agents available to use in epoxy systems, the characterization/quantification of the reacted groups is important in order to understand the reaction and its outcomes, like the final product properties.

Thermal analysis and Fourier transform infrared spectroscopy (FT-IR) are among the most relevant characterization techniques and are used in most studies. Differential exploratory calorimetry (DSC) and FT-IR transmission, in the middle infrared region (MIR), are the most applied. Thermogravimetric analysis (TGA) can be used offline (without coupling techniques) or online (coupled with FT-IR, for example) to determine the degradation temperature of the system and for the characterization and identification of different CAs (Guilherme et al. 2017, Romão et al. 2006, 2003).

NIR transmission/liquid film analysis is used in some curing reactions, showing the spectrometric changes better when compared to MIR analysis, and detecting smaller curing agent content in the epoxy system (Romão et al. 2004). This fact accredits the NIR region for further studies in epoxy systems, especially in the transmittance mode (NIRA) which is less

explored. The NIRA technique uses reflection and transmittance modes (reflectance for solids and transmittance for liquids), in the NIR region, to obtain fast and accurate results, without requiring sample preparations and specific sample supports that are required when using conventional NIR transmission mode (PerkinElmer 2011).

In a recent study (Tao et al. 2020), aiming to improve the resistance of epoxy systems with triblock copolymer poly(methyl methacrylate)-b-poly(butyl acrylate)-b-poly(methyl methacrylate) (MAM), the curing reaction was evaluated by FT-IR spectroscopy, using attenuated total reflection (ATR). The band of epoxide group, at 915 cm^{-1} , was evaluated and it was observed that it completely disappeared after curing, suggesting that the reaction was complete. According to the authors (Tao et al. 2020), FT-IR studies showed that the addition of MAM does not affect the structure of the cured epoxy. However, other spectrometric changes resulting from these reactions could have been mentioned, such as the appearance of the C=O band around 1730 cm^{-1} .

In another study, Ahangaran et al. (2019) used a mercaptan with ester groups, pentaerythritol tetrakis (3-mercaptopropionate) (PETMP), as a CA for epoxy systems, in self-healing composites. The study used FT-IR analysis, also qualitatively, to characterize functional groups.

Although the publications cited show good results, to the best of our knowledge, there is a lack of studies that evaluate monofunctional mercaptans, linear or branched, in epoxy resins reactions with hardeners, in either MIR and NIR regions. Also few publications are available using transmittance in the NIR region (NIRA).

Even the most recent articles (Tao et al. 2020, US Patent 2020) do not focus on the evaluation of mercaptans and the validation of IR techniques, in two regions, to quantify the

reaction, nor do studies evaluate mechanical properties of these modified epoxy systems. Consequently, this paper contributes to the study of modified epoxy systems, especially those that may be used as thermal protection adhesives, in the aerospace sector.

The objective of this study therefore is to evaluate by FT-MIR and FT-NIR (using near infrared reflectance accessory - NIRA) the reaction of EP with the CA diethylenetriamine (DETA) and the addition of normal dodecyl mercaptan (called n-SH) and tert-dodecylmercaptan (called t-SH) as flexibilizers. Different spectral regions and ways of obtaining spectra were used to demonstrate spectrometric changes. Conversion data, reaction times and methodology errors were evaluated qualitatively and quantitatively. NIRA analysis show satisfactory results, especially when the reaction was conducted in a more controlled manner in samples with lower amine contents. Shore hardness and tensile tests of the cured epoxy systems confirmed the flexibilization of the cured epoxy system by the addition of mercaptans, indicating a lower crosslinking degree in the matrix.

MATERIALS AND METHODS

Materials and reaction conditions

Samples of EP based on bisphenol-A diglycidyl ether (DGEBA) were mixed with diethylenetriamine (DETA) and mercaptans in adequate proportions and conditions (time and temperature). Normal dodecyl mercaptan (n-SH) and tert-dodecylmercaptan (t-SH) were supplied by Oswaldo Cruz and Unigel, respectively. Systems were coded as: EP/n-SH/DETA (5:5:1), EP/n-SH/DETA (5:5:0.3), EP/n-SH/DETA (5:5:0.1), EP/n-SH (1:1), and EP/t-SH/DETA (5:5:0.1).

The reaction temperature for the epoxy systems was 122°C (Romão et al. 2004). Samples for the FT-IR analysis were collected at the initial

time t_0 and different reaction times. The selected systems were analyzed by the conventional MIR transmission mode and in the NIR region by NIRA transfectance mode.

FT-IR analysis of EP/n-SH/DETA and EP/t-SH/DETA

The analyses were performed using a FT-IR NIR Frontier PERKINELMER spectrometer, with the following conditions: spectral region 4000 to 400 cm^{-1} (MIR) and 10000 to 4000 cm^{-1} (NIR partial spectral region), resolution of 4 cm^{-1} , gain 1 and 40 scans.

EP, DETA and mercaptan mixtures were prepared as liquid films, between two KBR windows, cured in an oven, in proportions, temperature and time already specified. Then they were analyzed in the MIR region, by transmission. For the NIR analysis (NIRA), the samples were prepared as liquid films, using Becher and a cylindrical metallic device to maintain thickness and reflection conditions, under the same previous curing conditions and then analyzed by transfectance.

FT-IR data used to evaluate the epoxide ring consumption were tabled using the average of two or median of three values obtained from different runs of the same reaction composition, with their respective standard deviation coefficients, calculated for each reaction time (Horák & Vitek 1978, Dutra 1984).

The analytical MIR band selected was the absorption around 915 cm^{-1} , assigned to the vibration of the epoxide ring. This band is widely used as the analytical band to study epoxy reactions independently of which CA is used. Its intensity was evaluated using the baseline 948 - 884 cm^{-1} . The band at 1384 cm^{-1} , assigned to the symmetrical deformation of the CH_3 group of the carbon chain, was used as reference to establish the relative band A_{915}/A_{1384} . Relative bands are used to compensate possible variations in

sample thickness along the reactions, in order to increase accuracy and achieve lower relative errors in the developed methodology (Dutra 1984).

According to the Lambert-Beer law, $A = a.b.c$ (Smith 1979), the absorbance intensity (a) is influenced by the thickness (b) and the concentration of the sample (c). Therefore, the greater the thickness of the sample the greater the absorbance intensity.

A relative band consists of the ratio between two analytical bands from the same spectrum. The use of a relative band is recommended because small thickness variations in a specific sample may occur during the reaction due to the movement of the sample support. The division of the bands cancels the thickness factor, avoiding distortions in absorption intensities of the analytical bands. By suppressing this thickness variation effect, it is possible to compare consumptions of the epoxy ring with more accuracy (Dutra 1984).

The selected analytical band for the analysis in the NIR region (NIRA) was the absorption at 4527 cm^{-1} , also commonly used to study epoxy reactions. It can probably be assigned to the combination of the absorptions at 3050 cm^{-1} related to the stretching of the CH group of the oxirane ring, and the deformation of the CH_2 group at 1460 cm^{-1} (Romão et al. 2004).

The intensity of the NIR analytical band is assessed by the baseline $4594\text{-}4496\text{ cm}^{-1}$. The 4166 cm^{-1} band, probably assigned to the third overtone of the band at 1384 cm^{-1} (symmetrical angular deformation of the CH_3 group of the carbon chain), was used as reference band to constitute the relative band A_{4527}/A_{4166} (Romão et al. 2004).

Studies by Horák & Vitek (1978) and Dutra (1984) evaluated the error of the developed methodologies with non-parametric statistics applied to spectroscopic analysis. This

assessment has already been successfully applied in recent papers aerospace materials (Rigoli et al. 2019, Jesus et al. 2019), and in previous papers (Dutra et al. 1996, Dutra & Soares 1998).

Equations 1 to 3 show, respectively, the standard deviation, average standard deviation and relative error used in the calculations. Results of the relative errors were approximated to an integer number.

$$\hat{\sigma} = K_R \times R \quad (1)$$

R= higher - lower absorbance value

($K_R = 0.591$ for 3 results and 0.886 for 2 results)

$$\hat{\sigma}_{\hat{\mu}} = \frac{\hat{\sigma}}{\sqrt{n}} \quad (2)$$

$$\text{relative error (\%)} = \left(\frac{\hat{\sigma}_{\hat{\mu}}}{\mu} \right) \times 100 \quad (3)$$

The percentage (%) of the reacted epoxide ring was calculated (Equation 4), similarly to that used by Dutra (1984) in the study of aziridine ring opening reaction. Results were approximated to an integer number of percentage.

% of the reacted epoxide ring =

$$\left[\frac{(A_0 - A_t)}{A_0} \right] \times 100 \quad (4)$$

Mechanical properties

Specimens for mechanical tests were produced using polyurethane molds. The reaction components were weighted and added to a Becher in the following sequence: the EP first, then the mercaptan, and finally the CA. The reaction mixture was then subjected to an ultrasound cleaner (Delta Ultrasons) to remove bubbles, for 2 minutes at room temperature. The mixture was carefully poured into the

Several researchers studied the effect of crosslinking density on tensile strength, tensile modulus, and elongation at break. Increasing crosslinking density enhances tensile strength and tensile modulus but decreases elongation at break. Decreasing crosslink density by blending DGEBA with aliphatic, cyclo-aliphatic or reactive diluents results in lower tensile strength and tensile modulus (Bajpai & Wetzel 2019).

The EP/n-SH and the EP/t-SH reaction mixtures were analyzed by FT-IR (MIR-transmission and NIRA-reflectance). Two reactional features were evaluated: qualitative assessment of spectrometric changes and appraising of variations in the intensity of bands. Absorptions modifications are resultant from chemical structure alterations of the products during the reactions. The variation in the intensity of the main bands involved in the reactions are related to the epoxide group conversion. A methodology that allows adequate monitoring of the reaction, showing the main spectrometric changes (appearance, disappearance of bands) involved in the reaction, curing time, maximum

measured content of the reacted epoxide group consumed and methodology error is proposed.

The 5:5:1 EP/mercaptan/DETA ratio obtained from the study of Andrade et al. (2008) was adopted as the starting point.

FT-MIR/ transmission analysis of EP/n-SH/ DETA (5:5:1)

Romão et al. (2003), Smith (1979), Urbanski et al. (1977) and many other researchers have widely discussed FT-IR bands of DGEBA, amine, and mercaptan-based curing agents. This study focuses on the bands around 915 cm^{-1} , related to the vibration of the epoxide ring and 3460 cm^{-1} , assigned to the stretching of the OH group. The band at 915 cm^{-1} was chosen as the analytical band used to monitor the reaction because it is related to the consumption of the epoxide ring.

Figure 2 shows the FT-MIR/transmission spectra of the reaction mixture EP/n-SH/ DETA (5:5:1) at $122\text{ }^{\circ}\text{C}$ and different reaction times.

A rapid decrease in the intensity of the band at 915 cm^{-1} , related to the consumption of epoxide rings, is observed as the reaction progresses. After 10 minutes, the band intensity

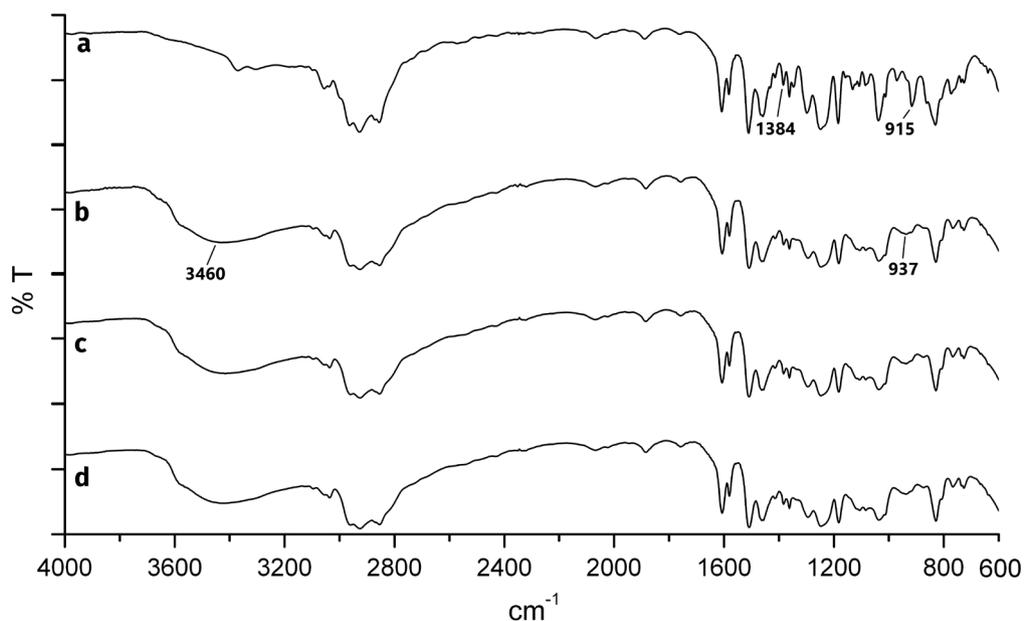


Figure 2. FT-MIR/transmission spectra (liquid film/sample as received) of the EP/n-SH/DETA reaction mixture (5:5:1), at $122\text{ }^{\circ}\text{C}$ and different reaction times (min): a) 0, b) 10, c) 60 and d) 120.

at 3460 cm^{-1} and 937 cm^{-1} increases significantly, indicating an increase in OH group content, which is due to the opening of the epoxide ring and formation of the hydroxyl group (Romão et al. 2004). Both spectrometric changes indicate a fast reaction.

Table I presents the FT-IR data for the reaction times that showed a difference in epoxide ring consumption, up to 120 min. It shows the calculated percentage (%) of the reacted epoxy rings, and the errors obtained in the FT-MIR/transmission of the EP/n-SH/DETA system (5:5:1).

Although the methodology presents a significant error of 17%, an increasing consumption of the epoxide ring is perceptible. After 20 min, the consumption of the epoxide rings reached 80%. Thus, the DETA content was reduced to evaluate the spectrometric changes and the measurements of the bands in a more controlled manner.

FT-MIR/ transmission analysis of EP/n-SH/DETA (5:5:0.3)

Table II displays the FT-IR data used to calculate the percentage (%) of the reacted epoxide rings

Table I. MIR/transmission (A_{915}/A_{1384}) results of the EP/n-SH/DETA (5:5:1) system, reacted at $122\text{ }^{\circ}\text{C}$.

Reaction Time - A_t (min)	Relative Band A_{915}/A_{1384}	Relative Band (median) A_{915}/A_{1384}	Average Standard deviation (*)	Relative deviation (%) (**)	Reacted epoxide rings (%) (***)	
0	$A_0 =$	1.955	2.426	0.296	12	0
	$A_0 =$	2.426				
	$A_0 =$	2.821				
10	$A_{10} =$	0.310	0.544	0.090	16	78
	$A_{10} =$	0.573				
	$A_{10} =$	0.544				
20	$A_{20} =$	0.290	0.439	0.078	18	82
	$A_{20} =$	0.519				
	$A_{20} =$	0.439				
30	$A_{30} =$	0.276	0.431	0.076	18	82
	$A_{30} =$	0.500				
	$A_{30} =$	0.431				
60	$A_{60} =$	0.300	0.429	0.068	16	82
	$A_{60} =$	0.500				
	$A_{60} =$	0.429				
120	$A_{120} =$	0.258	0.421	0.079	19	83
	$A_{120} =$	0.491				
	$A_{120} =$	0.421				
Methodology error (****) =					17%	

(*) (**) (***) - Equations 1 to 4 (Horák & Vitek 1978, Dutra 1984).

(****) Methodology error = median of the relative deviation (Dutra et al. 1996).

and the errors involved in the MIR/transmission methodology of the EP/n-SH/DETA system (5:5:0.3). The same spectrometric changes were observed as in the previous system.

Although 13% is considered a high methodology error, an increasing consumption of the epoxide ring was verified. After 20 min, the consumption of epoxide ring was already around 50% and continued to increase up to 77% after 420 min.

FT-MIR/ transmission analysis of EP/n-SH/DETA (5:5:0.1)

As observed in the previous systems, the EP/n-SH/DETA (5:5:0.1) system presented the same spectrometric changes. After 420 minutes, the consumption of the epoxide ring was around 47%, and after 1500 min it evolved to 70%. These findings suggest that this DETA content may be more suitable, since the reaction occurs in a more controlled way. It also increases methodology accuracy and allows better evaluation of the

spectrometric changes of the reaction by MIR/transmission.

The methodology error calculated for this system is shown in a future topic when comparing MIR and NIRA systems.

Figure 3 compares the reaction of the epoxide rings vs. time for different DETA contents. It is quite noticeable how the reaction rate depends on the amount of the CA DETA.

FT-MIR/transmission analysis of EP/n-SH (1:1)

The EP/n-SH (1:1) system was evaluated to verify whether the mercaptans would react with de DGEBA prepolymer in the absence of DETA.

Figure 4 shows the FT-MIR/transmission spectra (liquid film/sample as received) of the EP/n-SH (1:1) system at 122 °C, in different reaction times, qualitatively, showing the disappearance of the analytical band (915 cm⁻¹), after 25 hours and the appearance of other bands due to the reaction.

Table II. Resumed MIR/transmission (A_{915}/A_{1384}) results of the EP/n-SH/DETA (5:5:0.3) system, reacted at 122 °C.

Reaction time (min)	Relative Band A_{915}/A_{1384} (median)	Average Standard deviation (*)	Relative deviation (%) (**)	Reacted epoxide rings (%) (***)
0	2.923	0.006	1	0
20	1.497	0.021	1	49
30	1.148	0.150	13	61
90	1.068	0.165	15	63
120	0.997	0.143	14	66
210	0.899	0.127	14	69
240	0.789	0.009	1	73
360	0.747	0.099	13	74
420	0.672	0.067	10	77
Methodology error (****)=				13%

(*) (**) (***) - Equations 1 to 4 (Horák & Vitek 1978, Dutra 1984).

(****)Methodology error = median of the relative deviation (Dutra et al. 1996).

The epoxy ring band intensity at 915 cm^{-1} decreases and OH bands intensities at 3460 cm^{-1} and at 937 cm^{-1} increases, demonstrating the consumption of the epoxide rings, but in a much lower rate. The methodology error for this system was 9%, which was calculated using the same equations and same methodology as in all systems.

The methodology developed to study the reaction, in the MIR region, presented a series of peculiarities that made it difficult to properly employ.

The epoxy reaction leads to crosslinking and increases adhesion and therefore, over time, the liquid samples cure and stick to the KBr windows firmly attaching them. Since we performed each reaction twice or more times, many expensive pairs of KBr windows were damaged. Due to these difficulties, less expensive NIRA analysis was used to validate the results.

FT-NIRA/transflectance analysis of EP/n-SH (1:1)

Figure 5 shows partial FT-NIRA/transflectance spectra (6300 to 4300 cm^{-1}) of the EP/n-SH (1:1) system at $122\text{ }^{\circ}\text{C}$, at different reaction times.

The bands at 4527 cm^{-1} and 6063 cm^{-1} disappears after only 288h (twelve days), indicating a low reaction rate. The band at 4527 cm^{-1} is probably assigned to the combination of the absorptions at 3050 cm^{-1} (stretching of the CH group of the oxirane ring) and at 1460 cm^{-1} (bending of the CH_2 group) (Romão et al. 2004). The band at 6063 cm^{-1} is probably assigned to the first overtone of the vibration of the axial deformation of the CH group of the oxirane ring, around 3050 cm^{-1} (Romão et al. 2004).

NIRA analysis shows the intensity variation of two bands related to the epoxide ring, but the higher intensity of the band at 4527 cm^{-1} allows a better evaluation of the epoxide ring consumption.

Table III shows the NIRA/transflectance data, the error calculated for the methodology and the percentage (%) of reacted epoxide rings.

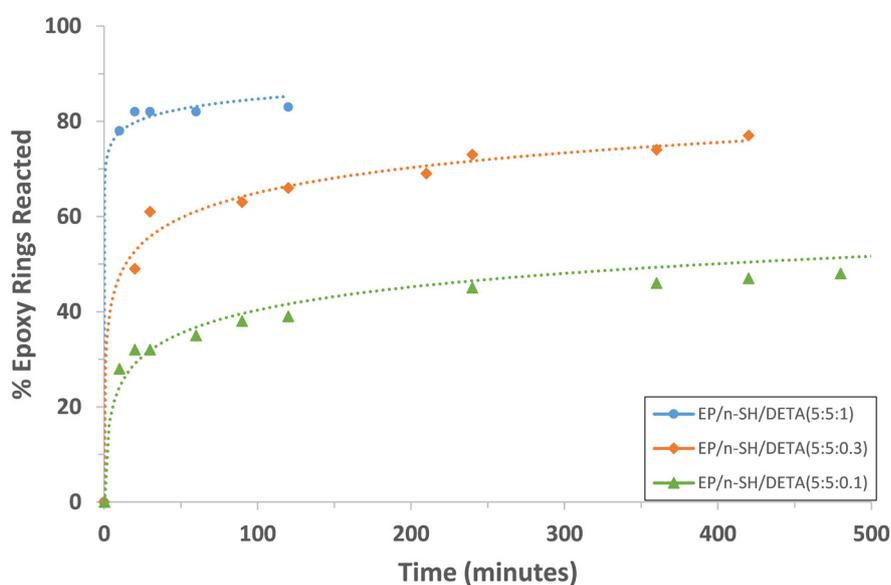


Figure 3. Epoxy rings reacted vs. time for EP/n-SH/DETA (5:5:1), EP/n-SH/DETA (5:5:0.3) and EP/n-SH/DETA (5:5:0.1) systems, at $122\text{ }^{\circ}\text{C}$, analyzed by FT-MIR (transmission).

No significant variation in the intensity of the analytical band A_{4527} was observed up to 300 min, demonstrating a low percentage of epoxide rings reacted, and after 2880 min only 33% of epoxide rings reacted. The methodology error of 4% is lower than those observed in the MIR methodologies for the same system (9%), suggesting that with the appropriate adjustments the NIRA/transflectance methodology may be more precise in the monitoring of these epoxy reactions.

The methodology error of 4% is acceptable considering that the precision limit of the equipment is $\leq 2\%$ (Horák & Vitek 1978, Dutra 1984) and is applicable under ideal conditions, with closed cell systems and ideal thickness control. The monitoring of the reaction is not viable using closed cell systems as it damages the cells. The relative band helps reducing the effect of the film thickness variation (Dutra 1984, Smith 1979), thus reducing errors.

The lower error of the NIRA methodology was expected as methodologies in the NIR

region have a greater quantitative merit (Dutra 1984, Azevedo et al. 2018, Karoui & Baerdemaeker 2007).

FT-NIRA/transflectance Analysis of EP/n-SH/DETA (5:5:0.3)

Table IV shows the FT-IR data of reaction times that displayed variations in epoxy ring consumption, the errors resulted from the NIRA/transflectance analysis of the EP/n-SH/DETA (5:5:0.3), and the estimated percentage (%) of reaction.

There is an increasing consumption of the epoxide rings. After 10 minutes 45% reacted, and after 24 hours (1440 min) almost 100% reacted. An increasing relative deviation (%) is observed during the reaction period due to the decrease in intensity of the analytical band which almost disappears because of the consumption of the epoxide groups.

The methodology error of 4% is quite satisfactory considering the analysis conditions.

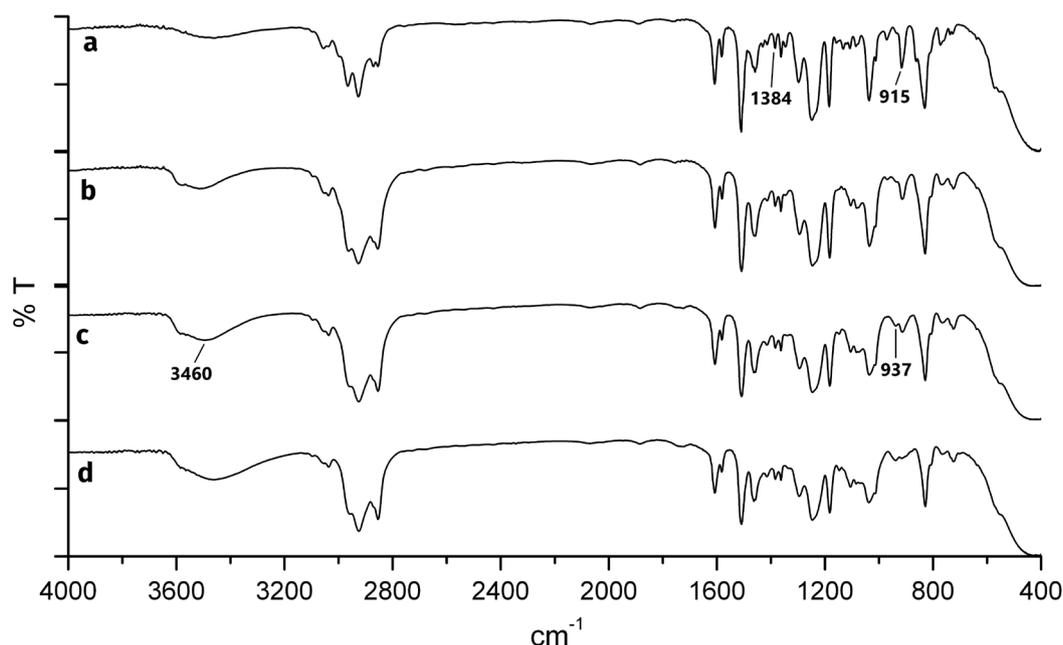


Figure 4. FT-MIR/transmission spectra (liquid film/sample as received) of the EP/n-SH system (1:1), at 122 °C, at different reaction times (h): a) 0, b) 1, c) 25, d) 182.

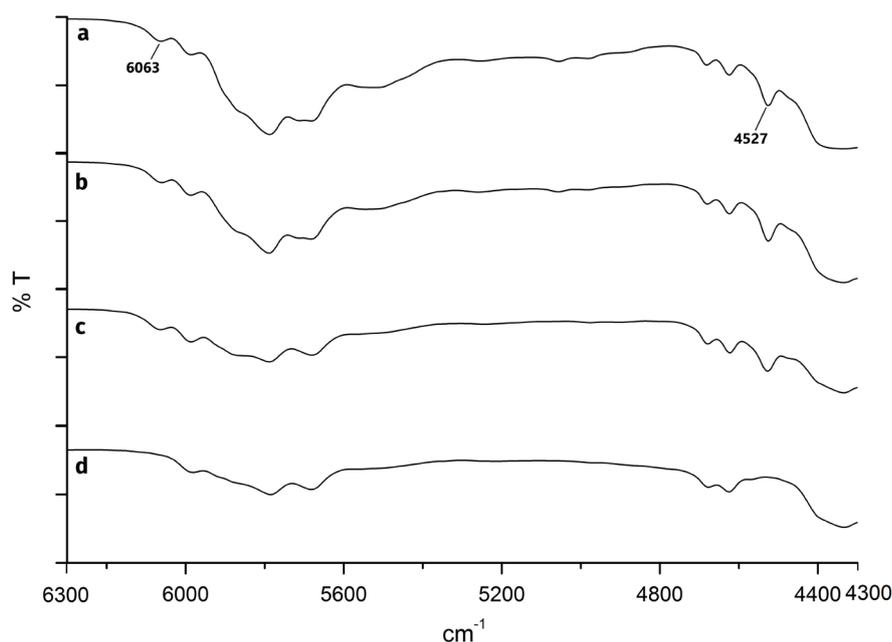


Figure 5. Partial FT-NIRA/transflectance spectra of the EP/n-SH (1:1) system at 122 °C, at different reaction times: a) 0h, b) 1h, c) 24h and d) 288h.

Table III. Resumed NIRA/transflectance (A_{4527}/A_{4166}) results of the EP/n-SH (1:1) system, reacted at 122 °C.

Reaction time (min)	Relative Band A_{4527}/A_{4166} (median)	Average Standard deviation (*)	Relative deviation (%) (**)	Reacted epoxide rings (%) (***)
0	2.082	0.021	1	0
300	2.054	0.070	3	1
360	2.043	0.024	1	2
420	2.000	0.093	5	4
1440	1.509	0.133	9	28
2880	1.400	0.089	6	33
Methodology error (****)=				4%

(*) (**) (***) - Equations 1 to 4 (Horák & Vitek 1978, Dutra 1984).

(****)Methodology error = median of the relative deviation (Dutra et al. 1996).

FT-NIRA/transflectance Analysis of EP/n-SH/DETA (5:5:0.1)

Regarding the EP/n-SH/DETA (5:5:0.1) system analyzed by FT-NIRA, the consumption rate of the epoxide ring reaches 80% after 24 hours (1440 min). The final methodology error obtained was 3%, which is quite satisfactory. It is interesting to note that the methodology error of 3% was the

same found in the MIR analysis for this same reaction system 5:5:0.1.

The behavior of this reaction in the proportion 5:5:0.1 in the MIR was very similar to that observed by NIRA, showing between 70 and 80% of conversion after 24 hours, as can be seen in Table V. This is the precision limit of the methodology, concerning the maximum content of epoxy reacted. These data also suggest that

the systems with 0.1 DETA content may be more suitable to evaluate spectrometric changes of the reaction by NIRA/transflectance since the reaction occurs in a lower rate and can be more accurately monitored.

FT-NIRA/transflectance analysis of EP/t-SH/DETA (5:5:0.1)

Due to the better results for the EP/n-SH/DETA systems obtained with 0.1 DETA content, these conditions were evaluated by using the branched mercaptan replacing the linear mercaptan in the EP/t-SH/DETA (5:5:0.1) system. The consumption of the epoxide ring reached 81% after 24 hours. The methodology error of 7% is satisfactory considering the analysis conditions.

Figure 6 presents the epoxy rings reacted vs. time for the different systems analyzed by

FT-NIRA (transflectance). It shows that systems containing t-SH and n-SH have similar behaviors.

FT-MIR (transmission) and NIRA (transflectance) data comparison

Table V shows MIR and NIRA absorptions and estimated percentage (%) of reaction of the epoxide rings for the EP/n-SH/DETA (5:5:0.1) system, analyzed by FT-MIR/transmission and FT-NIRA/transflectance, at 122 °C, as well as the calculated methodology errors.

MIR (A_{915}/A_{1384}) and NIRA (A_{4527}/A_{4166}) absorbances and the estimated percentage (%) of reaction of the epoxide rings were compared for the EP/n-SH/DETA (5:5:0.1) system, and are shown in Figure 7.

The linearity of $R=0.93$ and $R^2=86\%$ demonstrates the reasonable agreement of the FT-MIR/transmission and FT-NIRA/

Table IV. Resumed NIRA/transflectance (A_{4527}/A_{4166}) results of the EP/n-SH/DETA (5:5:0.3) system, reacted at 122 °C.

Reaction time (min)	Relative Band A_{4527}/A_{4166} (median)	Average Standard deviation (*)	Relative deviation (%) (**)	Reacted epoxide rings (%) (***)
0	2.009	0.079	4	0
10	1.105	0.038	3	45
20	1.074	0.042	4	46
30	1.026	0.035	3	49
60	1.037	0.033	3	48
120	1.000	0.036	4	50
240	0.833	0.034	4	59
300	0.761	0.043	6	62
360	0.716	0.045	6	64
420	0.672	0.076	11	67
1440	0.118	0.038	32	94
Methodology error (****)=				4%

(*) (**) (***) - Equations 1 to 4 (Horák & Vitek 1978, Dutra 1984).

(****)Methodology error = median of the relative deviation (Dutra et al. 1996).

transflectance absorbance values. This means that both methodologies estimate similar amount of epoxide groups reacted after each period and that the NIRA methodology may be used to estimate the reaction conversion.

There is a small divergence in the estimated conversion of the epoxy groups calculated using the experimental MIR and NIRA methodologies. The methodologies particularities and difficulties found for both systems justified the differences, as explained earlier. The difference is more significant as the reaction time increases because it is more difficult to read the relative band (A_{4527}/A_{4166}) in the NIR region. In this region, absorbance values are lower due to the scarce amount of remaining epoxide rings. This behavior was also observed in the reaction study of another aerospace resin: Carboxylated

polybutadiene (CTPB) with aziridine ring of the binding agent (Dutra 1984).

FT-IR methodology observations and precision limits

To develop FT-IR methodologies, many factors must be well controlled, for they may influence the result, such as collection times, preparation of reaction mixtures procedures, components weighing precision, homogenization of the samples that may vary due to the different component viscosities, time outside the oven to perform FT-IR analysis of samples, thickness of liquid films, among others.

In addition, the relative deviations of the infrared methodology tend to rise at the end of the reactions, when practically all the epoxide rings have been consumed. At this point, bands intensities become lower and affect significantly

Table V. MIR and NIRA absorbances, errors and estimated percentage (%) of reaction of the epoxide rings for the EP/n-SH/DETA (5:5:0.1) system, analyzed by FT-MIR/transmission and FT-NIRA/transflectance, at 122 °C.

Time (min)	Median Relative Band Absorbance		Relative deviation (%)		Reacted epoxide rings (%)	
	MIR (A_{915}/A_{1384})	(NIRA) (A_{4527}/A_{4166})	MIR (A_{915}/A_{1384})	(NIRA) (A_{4527}/A_{4166})	MIR (A_{915}/A_{1384})	NIRA (A_{4527}/A_{4166})
0	2.940	2.085	1	1	0	0
10	2.118	1.569	4	3	28	25
20	2.007	1.556	3	2	32	25
30	1.992	1.583	1	5	32	24
60	1.913	1.536	2	3	35	26
120	1.791	1.491	5	3	39	28
240	1.603	1.434	2	5	45	31
360	1.579	1.429	4	3	46	31
420	1.560	1.340	3	4	47	36
1440	0.882	0.422	17	55	70	80
Methodology error (****)=			3%	3%		

(****)Methodology error = median of the relative deviation (Dutra et al. 1996).

the relative deviation calculations. There is a precision limit for taking IR measurements (Smith 1979), in general between 20 and 80% of transmittance.

Considering these factors, the NIRA methodology precision limit allowed the monitoring of the reaction of EP/mercaptan/DETA systems, up to approximately one day of reaction and 80% of epoxide ring consumption, with methodology errors between 3 and 7%, which is very satisfactory considering the analysis conditions.

The reference value for the FT-IR methodology error of $\leq 2\%$ (Horák & Vitek 1978) is related to the precision limit of the spectrophotometer under ideal conditions of thickness control. This error limit is associated to quantitative FT-IR studies in the literature, generally applied to liquids analyzed by transmission in closed cells. The monitoring of epoxy reactions is not viable under these conditions as it damages the cells.

Nevertheless, higher error values have been accepted in the industrial field, including those obtained by transmission/pellet around 8% (Smith 1979), and by transmission NIR analysis

around 5% (Mello et al. 2018, Vogelsanger et al. 2014).

Evaluation of the mechanical properties

In order to evaluate the influence of n-SH and t-SH in the mechanical properties of the EP systems, 5 tensile test specimens were prepared as described in the experimental section for each system.

Figure 8 shows the stress-strain curves for the EP/n-SH/DETA (5:1:0.5) system reacted at 25 °C. The other stress-strain curves present similar behaviors.

A Shore D hardness test was performed for each specimen and then the specimens were subjected to tensile tests. Table VI shows the results from the mechanical tests.

Results showed that the hardness decrease when increasing the amount of mercaptan in the system. This increase of flexibility was also physically observed while handling the specimens.

Although standard deviations are significant, due to reasons explained below, Young modulus (E) and the ultimate tensile strength (σ_{max}) have

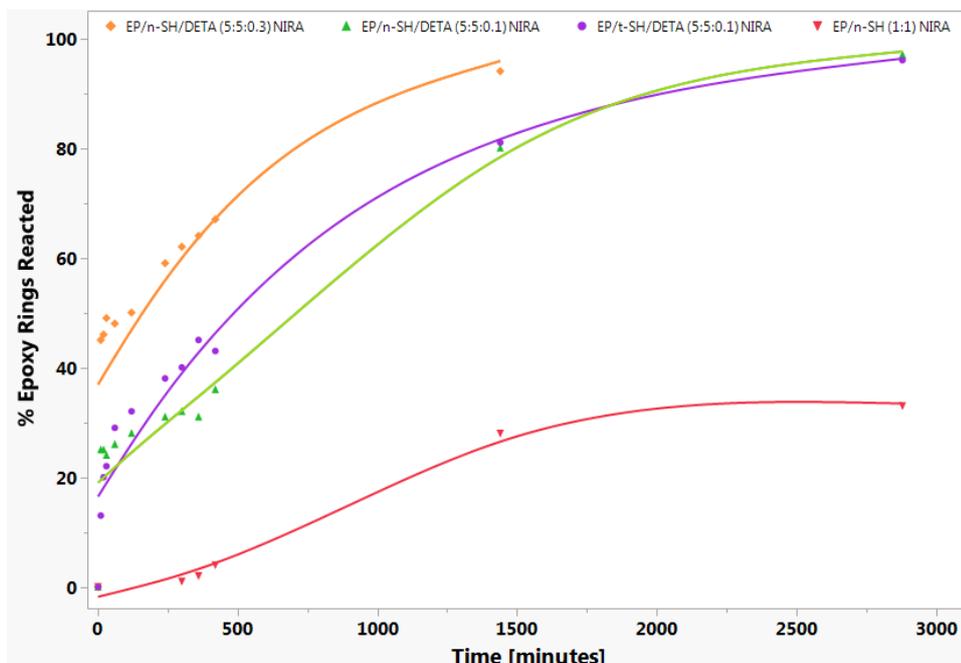


Figure 6. Epoxy rings reacted vs. time for EP/n-SH/DETA (5:5:0.3), EP/n-SH/DETA (5:5:0.1), EP/t-SH/DETA (5:5:0.1) and EP/n-SH (1:1) systems, at 122 °C, analyzed by FT-NIRA (transflectance).

a decreasing tendency, indicating that the stiffness of the solid material and the maximum stress to withstand stretching tend to decrease as the amount of flexibilizer n-SH increases in the system.

On the other hand, maximum elongation (ϵ_{\max}) tends to increase as the amount of mercaptan increases in the system, which is also an indication of flexibilization of the system.

Other compositions and temperatures were tested, but higher concentrations of mercaptan would not allow the curing and formation of the thermoset, nor lower DETA concentrations as 0.3 % would form the thermoset at room temperature. Higher temperatures were also explored using a curing cycle, gradually increasing temperature after curing stages until 122 °C. The curing process directly at 122°C was not suitable to produce tensile test specimens, since part of the components volatilized. The comparison of mechanical properties of epoxy systems containing mercaptans cured

at different temperatures may be further investigated in future papers.

Standard deviations are higher than those commonly observed in tensile strength tests, mainly due to difficulties in the preparation of the tensile specimens. Reaction mixture was poured into the polyurethane mold until cavities were filled, but the height of cured specimens did present small variances. Small bubbles and imperfections in the specimens were also observed, even though the use of the ultrasonic bath drastically reduced bubbles in the system.

Nevertheless, the final results of the compositions cured at 25 °C show a flexibilization tendency produced by the addition of n-SH and t-SH to the studied epoxy systems. Other mechanical tests, such as Dynamic Mechanical Analysis (DMA), may further explain the effect of the addition of mercaptans in epoxy systems, and can be the subject of future papers.

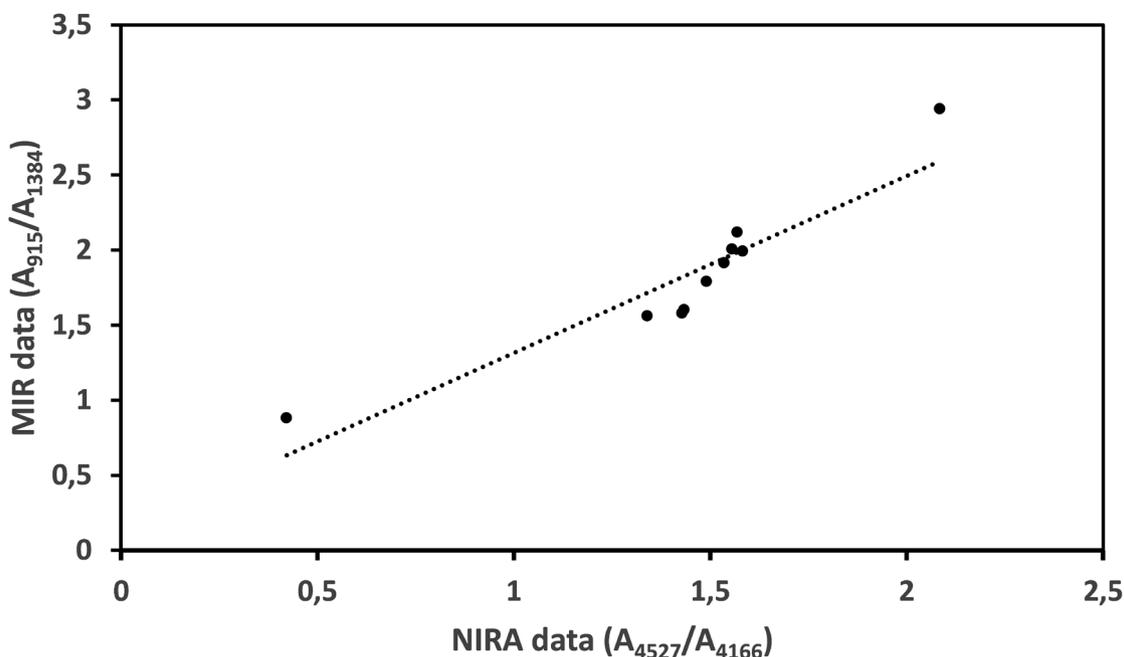


Figure 7. MIR absorbance values of relative band A_{915}/A_{1384} versus NIRA absorbance values of relative band A_{4527}/A_{4166} , used to estimate the content of epoxide groups reacted in the EP/n-SH/DETA (5:5:0.1) system at 122 °C.

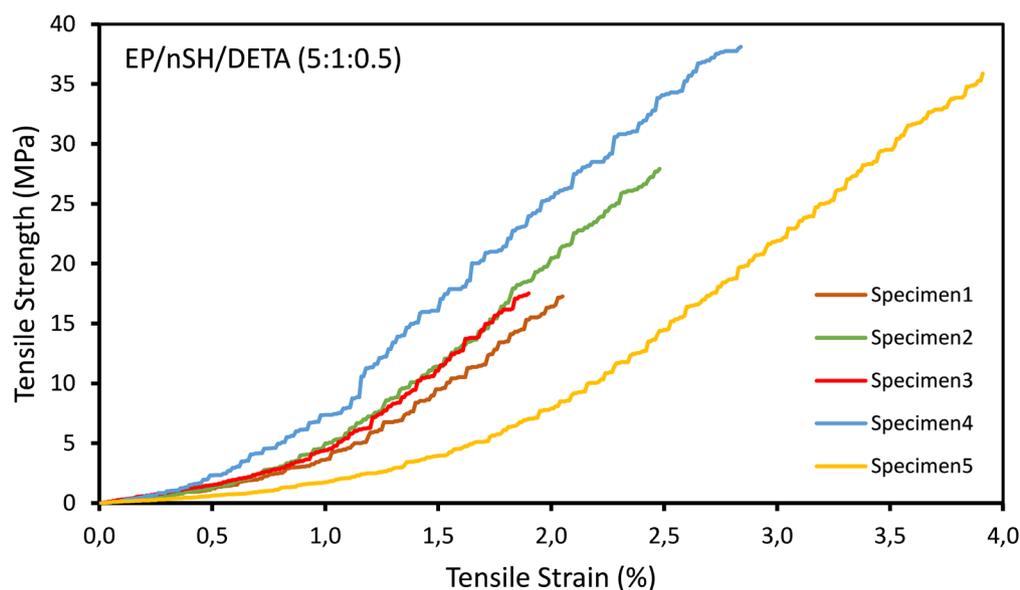


Figure 8. Stress-strain curves for the EP/n-SH/DETA (5:1:0.5) system reacted at 25 °C.

Table VI. Shore D hardness and tensile properties of epoxy-mercaptan-amine systems obtained from different samples and compositions, all reacted at 25 °C.

System	Hardness*	E [MPa]**	σ_{\max} [MPa]***	ϵ_{\max} [%]****
EP/DETA (5:0.5)	85 (\pm 1)	2017 (\pm 829)	29.32 (\pm 7.18)	1.44 (\pm 0.56)
EP/nSH/DETA (5:1:0.5)	78 (\pm 1)	578 (\pm 284)	27.34 (\pm 9.83)	2.63 (\pm 0.80)
EP/tSH/DETA (5:1:0.5)	80 (\pm 1)	534 (\pm 306)	19.83 (\pm 2.44)	2.25 (\pm 0.31)
EP/nSH/DETA (5:2:0.5)	73 (\pm 1)	471 (\pm 183)	23.40 (\pm 10.90)	2.76 (\pm 0.97)

(*) Shore D hardness, (**) Young modulus, (***) maximum tensile strength, (****) maximum elongation.

CONCLUSIONS

The NIRA accessory can be used to monitor and characterize the studied epoxy reactions, under appropriate conditions, reaching around 80% of reaction. This is the precision limit of the developed methodologies. The systems evaluated with this accessory presented satisfactory methodology errors, between 3 and 7%, better than most MIR methodologies.

It was possible to observe that when the amount of the curing agent DETA is increased,

the consumption of epoxide rings accelerates significantly.

A rather good agreement of the FT-MIR/transmission and FT-NIRA/transmittance absorbance values was observed for the EP/n-SH/DETA (5:5:0.1) system, analyzed at 122 °C. This particular system presented the best curing conditions and the lowest methodology errors (3%), for both MIR and NIRA methodologies.

Mechanical tests confirmed the flexibilization of the epoxy system with the addition of n-SH and t-SH to the system, indicating a lower crosslinking degree in

the matrix. Young's modulus (E) significantly decreased from 2017 MPa to 578 MPa with the addition of approximately 20% n-SH to the epoxy system, indicating less stiffness, still requiring though further investigations of the behavior of this flexibilizer in epoxy systems.

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